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For: SUBSTRATE WITH A PHOTOCATALYTIC COATING
Group Art Unit: 1771
Examiner: A.T. PIZIALI

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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
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To clarify the record, Applicants submit herewith a copy of Carneiro. This reference was originally cited in the response filed May 22, 2006.

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Study of the deposition parameters and Fe-dopant effect in the photocatalytic activity of TiO_2 films prepared by dc reactive magnetron sputtering

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Abstract

The reactive magnetron sputtering method was used to prepare pure and Fe-doped titanium dioxide thin films. The films were deposited onto microscope glass slides and polycarbonate plates at different total pressure and Fe-doping concentrations. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV-visible spectroscopy (UV). For glass substrates a polycrystalline TiO_2 structure was verified with X-ray diffraction, which showed typical characteristic anatase reflections. An iron phase appeared in the highly Fe-doped samples. The absorption edges of the Fe-doped TiO_2 films shifted to visible region with increasing concentration of iron. For the polycarbonate substrate an amorphous TiO_2 structure was revealed for all deposition conditions. The effects of different Fe-doping and total pressure levels on the photocatalytic activity were obtained by the degradation rates of Rhodamine-B (*RoB*) dye under UV light irradiation. For the deposition conditions considered in this study the highest photodegradation rates were achieved for films deposited on the polymer substrates. Of these overall highest rates was achieved for deposition at 0.4 Pa and without doping. However, for both substrates, films prepared at the particular total pressure of 0.5 Pa and a low iron concentration showed better photocatalytic activity than the pure TiO_2 films prepared under the same deposition parameters. On the contrary, the photocatalytic degradation rates of *RoB* on the highly Fe-doped TiO_2 films decreased strongly.

Keywords: Photocatalytic TiO_2 films; Fe-doping effect; Magnetron sputtering; Polycarbonate

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1. Introduction

In recent years, intense investigation has been performed on the TiO_2-assisted photochemical degradation of organic substances by UV radiation, either with the semiconductor catalyst in suspension or immobilized on a solid support to avoid further separation processes [1–11]. The method was originally contemplated as a possibility to employ solar radiation as an energy source in water decontamination processes in association with the treatment of industrial effluents (to avoid environmental damage) and water potabilization [5,11]. At a certain stage, studies have markedly shifted towards the use of artificial UV sources, mainly mercury vapour lamps, because of the low efficiency obtained with the solar radiation, the practical inconvenience of having to rely on the unpredictable availability of a natural light source and the poor overlapping of the solar spectrum with the TiO_2 absorption range [7].

Titanium dioxide occurs in three crystalline forms (rutile, anatase, and brookite), among which anatase is believed to be the most efficient photocatalyst during chemical reactions [12,13]. Most of the studies were focused on the nanosized TiO_2 in order to improve the light absorption: the high surface-to-volume ratio of nanograins is useful as has been reported in the literature [14]. Moreover, increasing the generation rate of charge carriers is one way to enhance the photocatalytic activity. This is centred on the formation of an electron–hole pair, respectively (e^-) and (h^+), on the TiO_2 surface upon the incidence of a photon with energy equal to or higher than the gap between the valence and the conduction band within the semiconductor crystal. On the other hand, electron and hole trapping during their movement from the interior of the particle to the surface is also very important for preventing the recombination of electron hole pairs. Doping of TiO_2 with transition metal ions [15] gives a way to trap charge carriers and extend the life time of one or both of the charge carriers.

TiO_2 films have been prepared by a variety of deposition techniques such as sol–gel process, colloid baking, chemical vapour deposition, evaporation and various reactive sputtering depositions [16–18]. The aim of this research is to study the effect of some deposition conditions such as, the total deposition pressure and the amount of Fe-metal dopant on the efficiency of the photocatalytic process of TiO_2 thin films prepared by dc reactive magnetron sputtering (MS). MS can be used to prepare good quality films because it is a friendly environment industrial process which can be applicable to large-area deposition or even when large-scale production is needed.

Moreover, it must be noted that polymers have gained substantial interest as base materials in current industry. Polycarbonate is one of the newer thermoplastics used in the construction industry and in many automotive applications due to its excellent properties of impact resistance, low weight and transparency. Building roofs, building windows, car roof elements, automotive headlamps, cameras, ophthalmic lenses, optical sensors and other optical equipment are all convincing technological products which highlight the application of polymeric materials in industry. However, photocatalytic properties of TiO_2 films deposited on polycarbonate have rarely been reported in physical vapour deposition (PVD) industry.

2. Experimental procedure

Fig. 1 shows the schematic of a home made MS system used in the preparation of our TiO_2 films. The films were deposited both on glass and on polycarbonate slides ($75 \times 25 \times 1\,mm^3$). A 99.99% pure titanium target with a diameter of 10 cm and a total area (TA) of about $7854\,mm^2$ was used. The distance between target and substrate was 60 mm.

After the chamber was evacuated to a base pressure lower than 1×10^{-3} Pa, a 99.99% pure argon sputtering gas was introduced into the chamber and discharge began at a constant current of 0.2 A. After the discharge voltage stabilized at a low value, 99.5% pure oxygen gas was introduced into the chamber at a constant oxygen flow rate of 2.5 ml/min to participate in the chemical reaction to form TiO_2. Titanium dioxide thin films were prepared at two different total sputtering pressures, that is 0.4 and 0.5 Pa. The reason why this

small pressure range was chosen is concerned with the objective to investigate the photocatalytic sensitivity of TiO_2 films (translated by eventual changes in the photodegradation rate) deposited under small variations in total sputtering pressure. For all films, an average film thickness of about 600 nm (evaluated by SEM) was obtained by changing the deposition time under different total sputtering pressure.

The iron pieces ($5 \times 5 \times 0.2\,mm^3$) with purity of 99.9% were placed on the titanium target in order to promote the film doping effect. The colour of the films changed from light white to light yellowish and finally to dark yellowish following the sequence from pure titanium dioxide to the higher iron concentration. The typical deposition parameters and the *iron piece area* (IpA) used for doping TiO_2 films are shown in Table 1.

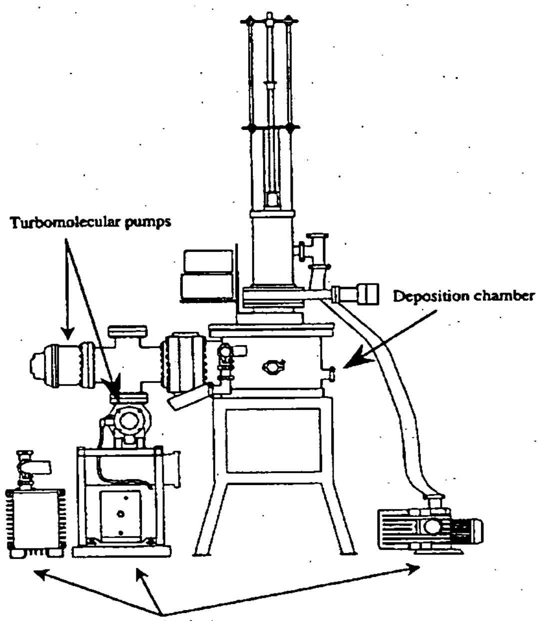

Fig. 1. Schematics of reactive magnetron sputtering system for coating deposition.

X-ray diffraction (XRD) analysis was carried out for all samples. XRD 2θ scans were recorded by using CuK_α radiation source in a Philips PW 1710 BASED diffractometer for the characterization of the crystalline structure of the undoped and doped TiO_2 samples. Specific software was used to measure the precise 2θ positions and the full-width at half-maxima (FWHM) of the diffraction peaks. The crystalline grain size was calculated from the XRD pattern according to the Scherrer equation [18].

$$D_{hkl} = 9.94\,\lambda / B_{hkl} \cos\theta \qquad (1)$$

where D_{hkl} is the mean grain size with crystalline planes (hkl), B_{hkl} is the FWHM intensity in radians and λ is the wavelength of the CuK_α radiation source. The surface morphology of the films was observed by SEM in a LEICA Cambridge S360 instrument and AFM in a NANOSCOPE III, Digital instruments. The thickness of the films was evaluated by SEM. The optical transmission spectra of the films were measured with a Shimadzu UV-310PC scanning spectrophotometer.

The photocatalytic activity of undoped and Fe-doped TiO_2 thin films was characterized with the decomposition rate of an aqueous solution of Rhodamine-B on the films by UV irradiation. Rhodamine-B ($C_2H_{31}ClN_2O_3$) is a strongly red fluorescent dye with a molecular weight of 479. It is a chloride salt that dissociates in aqueous

Table 1
Deposition parameters and iron piece area on titanium target in the deposited TiO_2 films

Code sample	A	B	C	D
Iron piece area: IpA (mm^2)	—	—	50	200
(Iron piece/titanium target) ratio area: (IpA/TA) %	—	—	0.64	2.5
Ar flow rate (ml/min)	17.4	19.0	19.0	19.0
Total pressure-P_{total} (Pa)	0.4	0.5	0.5	0.5

solution, leaving a positive charge on one of the nitrogens. In each run, a TiO_2 film of $1.0 \times 1.5\,cm^2$ was placed in a quartz cell probe, which contained 10 ml aqueous *RoB* solution with a concentration of 0.5 mg/l. The UV source was a mercury tube lamp irradiating a wavelength of 254 nm. The film was irradiated in a perpendicular direction and the distance between the film and the UV source was 11 cm. The photodegradation efficiency was monitored by measuring transmittance at the wavelength of 554 nm using a Shimadzu UV-310PC scanning spectrophotometer. The transmittance of the solution was measured at 15 min intervals for a total irradiation time of about 90 min.

3. Results and discussion

3.1. Structural characterization

In Fig. 2 we present the evolution of TiO_2 film X-ray spectra for the samples prepared with different deposition parameters and deposited on the glass substrate.

It can be observed that crystallinity of our films increases for the lowest pressure values. Only the anatase phase was identified in the undoped films. The polycrystalline anatase structure was confirmed by the (1 0 1) and (0 0 4) diffraction peaks, and also the traces of (2 0 0), (1 0 5) and (2 1 1) peaks. However, they had the preferred orientation of the anatase (0 0 4) plane, although the intensity was lower for the pure TiO_2 deposited at higher pressures. For samples with addition of dopant, the films had an amorphous structure.

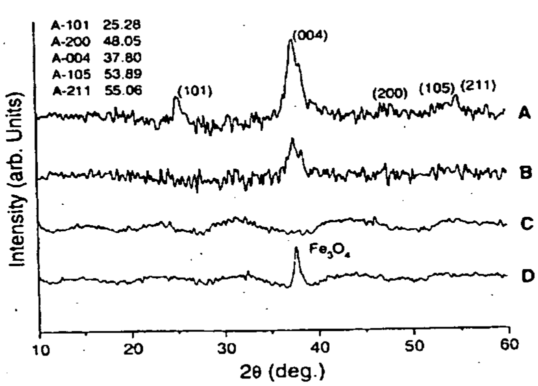

Fig. 2. XRD patterns of undoped and Fe-doped TiO_2 films deposited on glass. The deposition conditions A, B, C and D are given in Table 1.

There were no Fe-dopant-related peaks in the XRD patterns for sample C. The Fe_3O_4 phase appeared in sample D, which contained the higher iron concentration. Based on the full width at half maxima of the XRD peaks, the average particle diameter was calculated to be about 4.1 ± 1 and 7.1 ± 1 nm respectively for samples A and B. For all samples deposited on the polycarbonate substrate only an amorphous structure was apparent from the XRD spectra.

3.2. Surface characterization

The evolution of the surface with deposition conditions was followed by SEM and AFM techniques, respectively. SEM micrographs show images of the surface morphology of the pure TiO_2 films deposited at different total pressures in the sputtering deposition chamber [see Fig. 3(a)–(b)]. The films were mainly composed of small spherical particles. The surfaces of the films exhibited a certain degree of roughness and the film became rougher when total pressure was higher during deposition.

Atomic force micrographs presented in Fig. 4(a)–(b) come, respectively, from the pure titanium dioxide (sample B) and the Fe-doped TiO_2 (sample D) in which iron area percentage (IpA/TA) was equal to 2.5%.

An increase in surface roughness (at nanometre level) and size of the top columnar growth with lower structural densification is observed for the higher Fe-doped sample D. The iron went into substitutional sites of the TiO_2 crystal structure. The position of the dopant is determined by size differences between the host Ti^{4+} ionic radius and the dopant ionic radius. From the effective radius of ions for a coordination number 6 [19], one can see that Fe^{3+} ion has a small ionic radius (0.645 Å) that is comparable to that of Ti4+ (0.605 Å). Thus, it is energetically favourable for this ion to

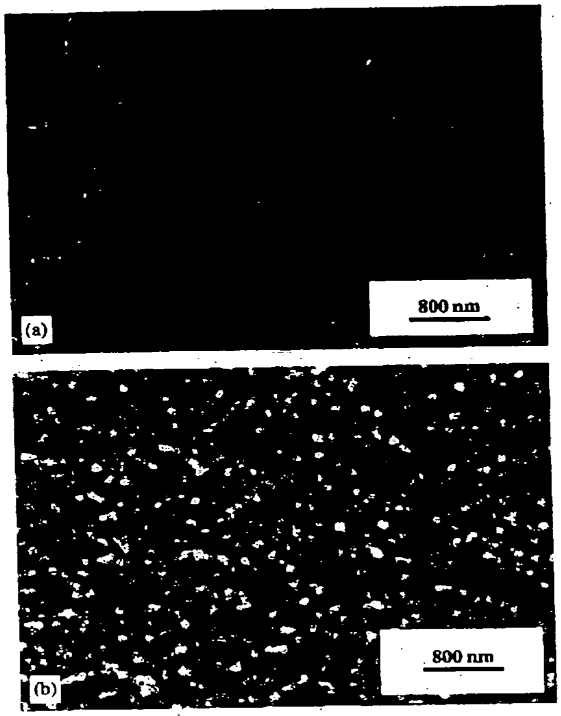

Fig. 3. SEM images of pure TiO_2 films: (a) sample A, (b) sample B.

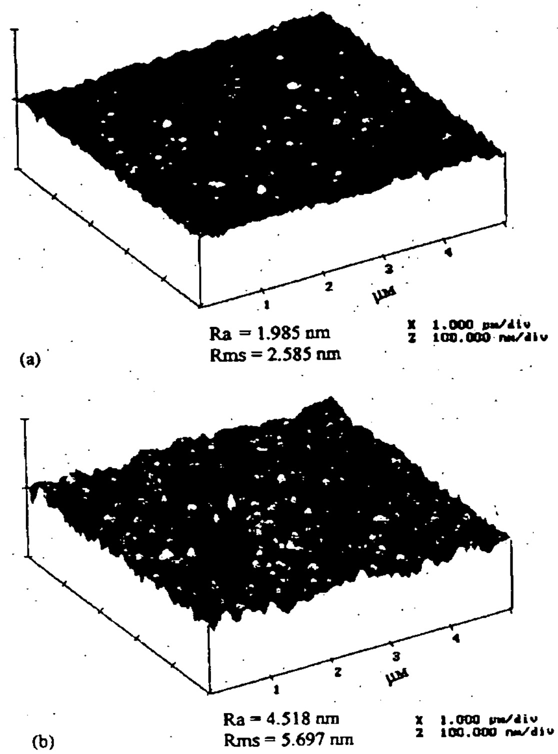

Fig. 4. AFM images of pure and Fe-doped TiO_2 films: (a) sample B, (b) sample D.

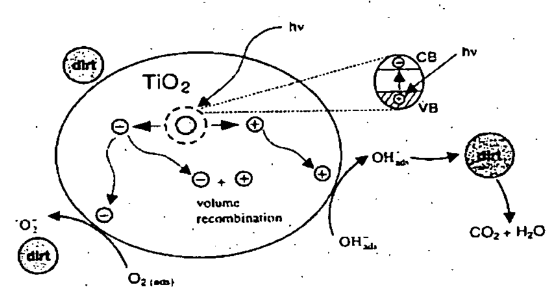

Fig. 5. Initial redox events subsequent to hole and electron trapping.

occupy Ti^{4+} sites. However, if the iron concentrations are far more than its solubility in TiO_2 then an iron oxide surface enrichment is expected, leading to the formation of bigger particles and surfaces with higher roughness.

3.3. Photocatalytic activity

The photocatalytic mechanism is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO_2 ($\approx 3.23\,\text{eV}$ in anatase phase) [1–8] producing an electron–hole pair on the TiO_2 surface as schematized in Fig. 5.

An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). In order for this process to have a net chemical effect, the volume recombination of the electron–hole pair has to be precluded. The natural fate for h^{+}_{VB} and e^{-}_{CB} is the removal of either of them by means of redox reactions involving the organic compounds adsorbed on the semiconductor surface. The standard chemical

reactions have been reported by other authors [20,21]:

$$TiO_2 + h\upsilon \rightarrow e^-_{cb} + h^+_{vb}, \quad (2)$$

$$e^-_{surf} + O_{2(ads)} \rightarrow {}^{\bullet}O_2^-, \quad (3)$$

$$h^+_{vb,surf} + OH^-_{(ads)} \rightarrow HO^{\bullet}_{(ads)}, \quad (4)$$

$$HO^{\bullet}_{(ads)} + \text{dirt} \rightarrow \rightarrow xCO_2 + yH_2O. \quad (5)$$

Hydroxyl radicals ($HO^{\bullet}$) and super-oxide ions (O_2^-) are highly reactive species that will oxidize the organic compounds adsorbed on the semiconductor surface. The number and lifetime of free (e^-/h^+) pair are particle size and dopant-dependent [22]. For large particles, the (e^-/h^+) volume recombination is the dominating process. In fact, for small sized particles the covered distance by (e^-/h^+) pair during their movement from crystal interface to the surface is short, which increase the migration rate to the surface of the small size particle in order to participate in the chemical reaction. Besides the effect of particle size on the photocatalytic activity, the role of a metal ion dopant is also very important because it can act as an electron trap in the semiconductor interface. The trap of charge carriers can decrease the volume recombination rate of (e^-/h^+) pairs and thus increase the lifetime of charge carriers. The process of charge trapping is as follows [22]:

$$M^{n+} + e^-_{cb} \rightarrow M^{(n-1)+}, \quad (6)$$

where M^{n+} is the metal ion dopant. The energy level of $M^{n+}/M^{(n-1)+}$ lies below the CB edge. Thus, the energy level of transition metal ions affects the trapping efficiency. The trapping of electrons makes it easy for holes to transfer onto the surface of TiO_2 and react with OH^- in the surface and form active $^{\bullet}OH$, hydroxyl radicals to participate in the degradation of dirt.

Fig. 6(a)–(b) shows the optical transmittance spectra of the series of TiO_2 thin films deposited, respectively, on glass and polycarbonate substrates.

In the visible range the transmission of spectra shows waveforms that are characteristic of light interference [23]. For both substrates, the absorption edges of Fe-doped TiO_2 films shifted to long wavelength when the amount of Fe-dopant increased, as shown in Fig. 6(a) and (b). This red shift has been attributed to the excitation of *3d* electrons of Fe^{3+} to the CB [24]. In fact, the main purpose of Fe doping is to extend the light absorption edge in order to make use of the majority of the ambient light spectrum. The absorption edge of sample C shifted to 380 nm near to the visible region and the sample D shifted to 450 nm in the visible region.

The influence of different total pressures in the photocatalytic activity of the series of pure TiO_2 thin films (deposited on glass and polycarbonate substrates) were examined and are shown in Fig. 7(a) and (b).

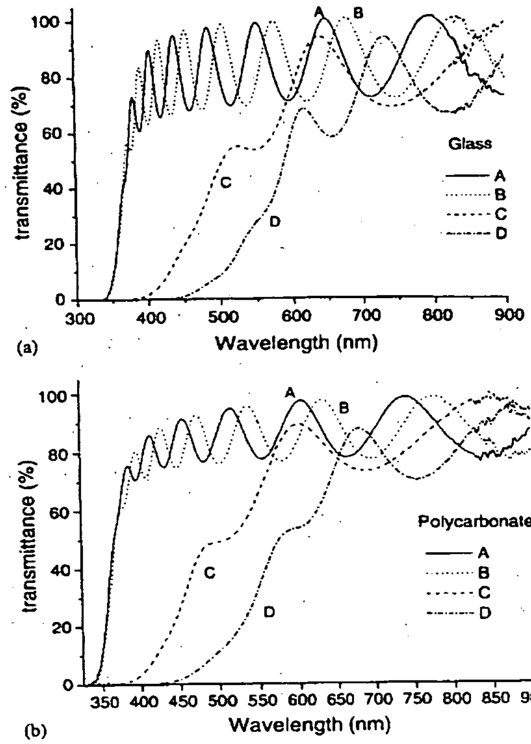

Fig. 6. UV-vis spectra of pure and Fe-doped TiO_2 films prepared by dc reactive magnetron sputtering at different total pressures. On different substrates: (a) on glass and (b) on polycarbonate.

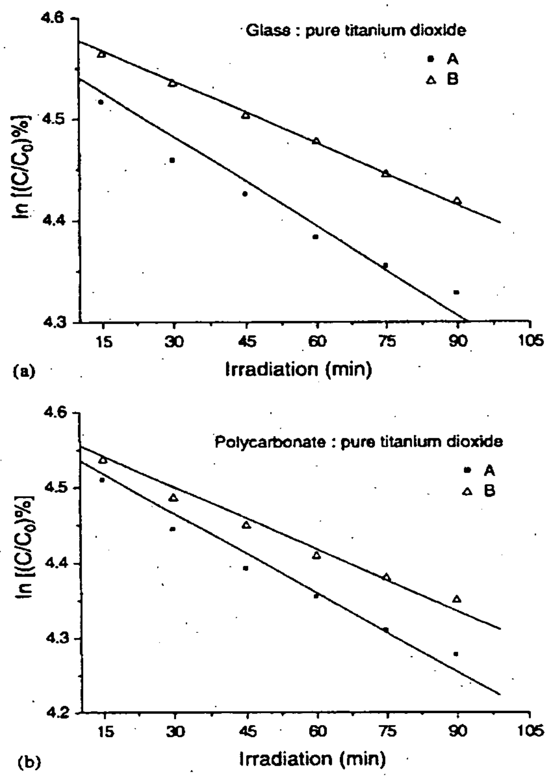

Fig. 7. Effect of different total pressures in the photocatalytic degradation of *RoB* dye on the pure TiO_2 films deposited on different substrates: (a) on glass and (b) on polycarbonate.

The photodegradation of *RoB* dye follows the kinetic first-order reaction [25]:

$$\ln\frac{C}{C_0} = -kt, \tag{7}$$

where C_0 is the initial concentration of *RoB* aqueous solution, C is the concentration measured at the end of a particular interval of time, and k is the apparent photodegradation rate constant.

The Photocatalytic activities can be compared by using k values which can be obtained from the slopes of the fitting lines in Fig. 7. It is observed that, for both substrates, the photocatalytic activity of the undoped TiO_2 films deposited at the lower total sputtering pressure (0.4 Pa) is increased. Possible explanations could be based on the difference of the TiO_2 particle sizes which were obtained under different total sputtering pressures. In fact, the measured grain sizes were 4.1 ± 1 and 7.1 ± 1 nm, respectively, for samples A (deposited at 0.4 Pa) and sample B (deposited at 0.5 Pa). Thus, this indicates that smaller particles enhance the photocatalytic activity, consistent with the findings of other authors [22]. In fact, as the grain size is decreased the surface-to-volume ratio is increased; the transportation length of the e^-/h^+ pair from crystal interface to the surface is short and the e^-/h^+ volume recombination rate is decreased which would lead to an improvement in the photocatalytic activity.

Fig. 8(a) and (b) is the comparison of the *RoB* dye photodegradation activity for pure and Fe-doped TiO_2 samples with different iron concentrations and deposited at the same total pressure (0.5 Pa).

For both substrates the change of the photocatalytic activity for Fe-doped samples is evident from the slopes of the photodegradation curves. When compared with the pure TiO_2 films (samples B) the photodegradation rates of the moderate Fe-doped TiO_2 films (samples C) have been slightly enhanced. On the contrary, high iron concentration (samples D) was detrimental for photocatalytic activity as evidenced in Fig. 8(a) and (b) by the lower gradient slopes of the fitting curves. Fig. 9 plots the numerical values of the apparent photodegradation rate constant for all TiO_2 thin films deposited on glass and polycarbonate substrates.

From Fig. 9 it can be seen that, for both substrates and for all TiO_2 samples (i.e. prepared with different deposition conditions), the photocatalytic degradation rates of *RoB* dye on the highly Fe-doped TiO_2 films decreased abruptly with increase in iron concentration (samples D). The optimum Fe-doping concentration can be explained by the balance of an increase in trapping sites leading to efficient trapping and fewer trapped carriers leading to longer lifetimes for interfacial charge transfer [26]. At concentrations below the optimum value, photocatalytic activity should increase with an increase of the iron

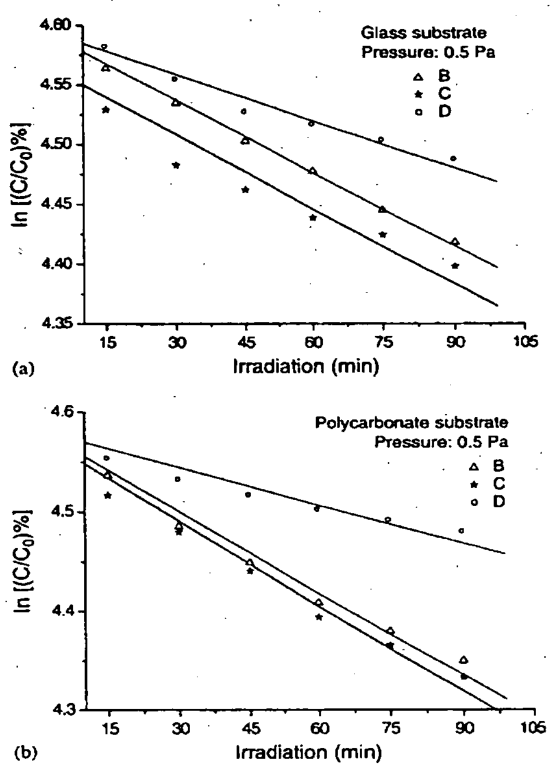

Fig. 8. Photodegradation of *RoB* dye with undoped TiO_2 and Fe-doped TiO_2 under UV light source: (a) on glass substrate and (b) on polycarbonate substrate.

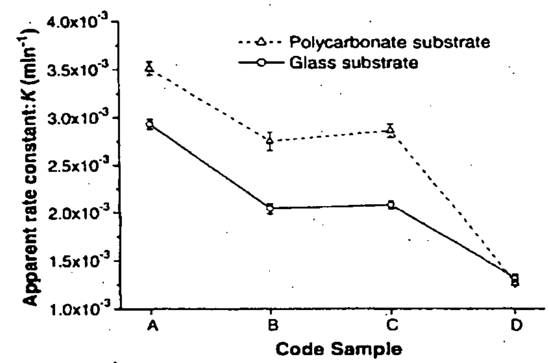

Fig. 9. Apparent photodegradation rate constant k for all TiO_2 thin films prepared under different deposition conditions .Comparison between glass and polycarbonate substrates.

concentration because there are fewer trapping sites available. However, if the iron concentration is far more than its solubility in the TiO_2 structure then a decrease in photocatalytic activity should be expected as was observed.

It is also observed that for all TiO_2 thin films, the highest photodegradation rates were achieved for films deposited on the polycarbonate substrates in spite of their amorphous structure. Moreover, from our spectra transmittance results it can be observed that there is a wavelength range from about 350 nm to near visible region in which transmittance varies from about 10–70%. Thus, under this wavelength band our coatings do not absorb all the UV radiation. We believe that it can be possible that one fraction of transmitted UV radiation could promote some changes in the type of PC polymer molecular arrangement leading to an eventual enhancement in the photocatalytic activity. In spite of this, it is not yet clearly understood for us the main mechanisms under which the observed photocatalytic activity is stronger for films deposited on polycarbonate.

4. Conclusions

Transparent and uniform undoped and Fe-doped TiO_2 thin films were deposited on glass and polycarbonate substrates by dc reactive magnetron sputtering using different deposition parameters. The TiO_2 films deposited on the glass substrate showed the anatase crystal phase with a preferred orientation along the (0 0 4) plane. When the total pressure increased the intensity of the (0 0 4) peak decreased. The decrease of the 004 peak can be related with the mobility of the adatoms on the substrate surface that is lower for higher deposition sputtering pressure which in turn affects the type and rate of nucleation on the substrate leading to a different crystallinity. The grain sizes were 4.1 and 7.1 nm for the pure TiO_2 films deposited at total pressures of 0.4 and 0.5 Pa, respectively. On the contrary, for TiO_2 films deposited on the polycarbonate substrate an amorphous structure was observed.

The surface morphologies of the undoped and Fe-doped films changed from slight roughness to

rough, for undoped to highly Fe-doped TiO_2 films, respectively. For both substrates the absorption edges of the Fe-doped TiO_2 films shifted to longer wavelength up to visible region when the concentration of iron increased.

For undoped TiO_2 films, the aqueous Rhodamine-B degradation rate was enhanced when the total pressure on the deposition chamber decreased to 0.4 Pa. At this deposition pressure, the grain size is lower than that obtained at 0.5 Pa. For lower grain sizes, the transportation length of e^-/h^+ pairs from crystal interface to the surface is short resulting in an increase of the migration rate of e^-/h^+ pairs to the surface of the particle in order to participate in the reaction process. This could lead to an enhancement of the photocatalytic activity.

For both substrates, the films with the moderate iron concentration showed better photocatalytic activity than the pure TiO_2 film deposited under the same total pressure of 0.5 Pa.On the contrary, high iron concentration was detrimental for photocatalytic activity.

From our results, the photocatalytic activity was stronger for TiO_2 films (undoped and Fe-doped) deposited on the polycarbonate substrates since the photodegradation rates had an average increase of about 30%. Besides the possible UV radiation effect on changing the PC polymer molecular arrangement, we believe that another effect can contribute to the enhancement of photocatalytic activity. This effect can be related with the temperature increase and local structural changes on the PC polymer surface due to the electron and ion bombardment during the initial deposition steps. In fact, for the same volume, polycarbonate has lower mass and subsequently the PC surface might be at a higher temperature than the glass in the same deposition conditions. However, the nature of these interactions effects in the enhancement of the photocatalytic activity in coated polycarbonate is not yet clearly understood for us. Thus, further studies are necessary to perform for a fully understanding of the main mechanisms that are responsible for the enhancement of the observed photocatalytic activity in coated polycarbonate. Consequently, this study led us to the deposition of transparent TiO_2 films on polycarbonate with improved photocatalytic activity, which opens more perspectives for the industrial application of polymers as a low weight "self-cleaning" material.

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